

CO₂ Capture Systems Using Amine Enhanced Solid Sorbents



Thomas J. Tarka¹
Jared P. Ciferno²
McMahan L. Gray²
Daniel Fauth²

¹: Energetics, Incorporated

²: National Energy Technology Laboratory (NETL)

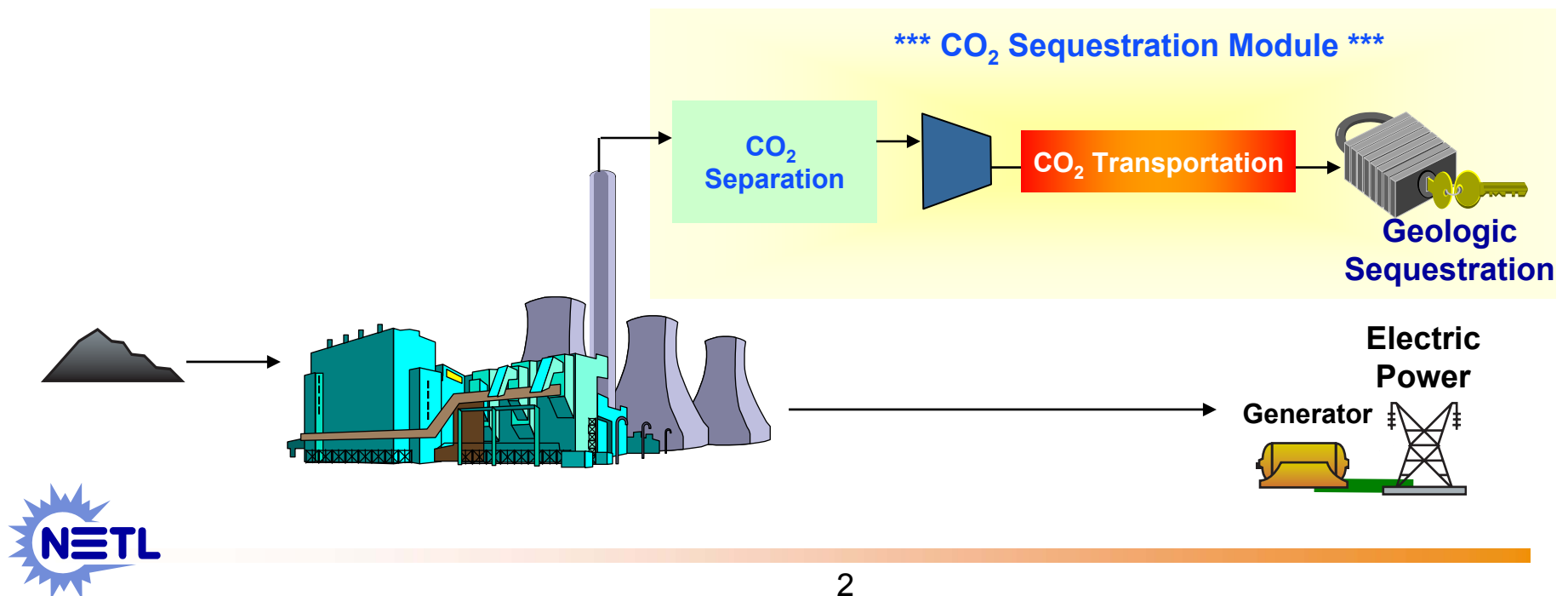
5th Annual Conference on Carbon Capture & Sequestration



Systems Analysis Objective

Analyze Detailed Component Costs for Capture & Storage to:

- **Determine where the R&D should be focused**
 - Includes both NETL in-house R & D and Externally Funded R & D
- **Determine “best case” potential for R&D technologies**



Systems Analysis Objective: Scale-Up

Laboratory Scale



- 0.1 ft³ Reactor Volume
- 0.27 scf per minute

Technically
Possible?

Scale-up

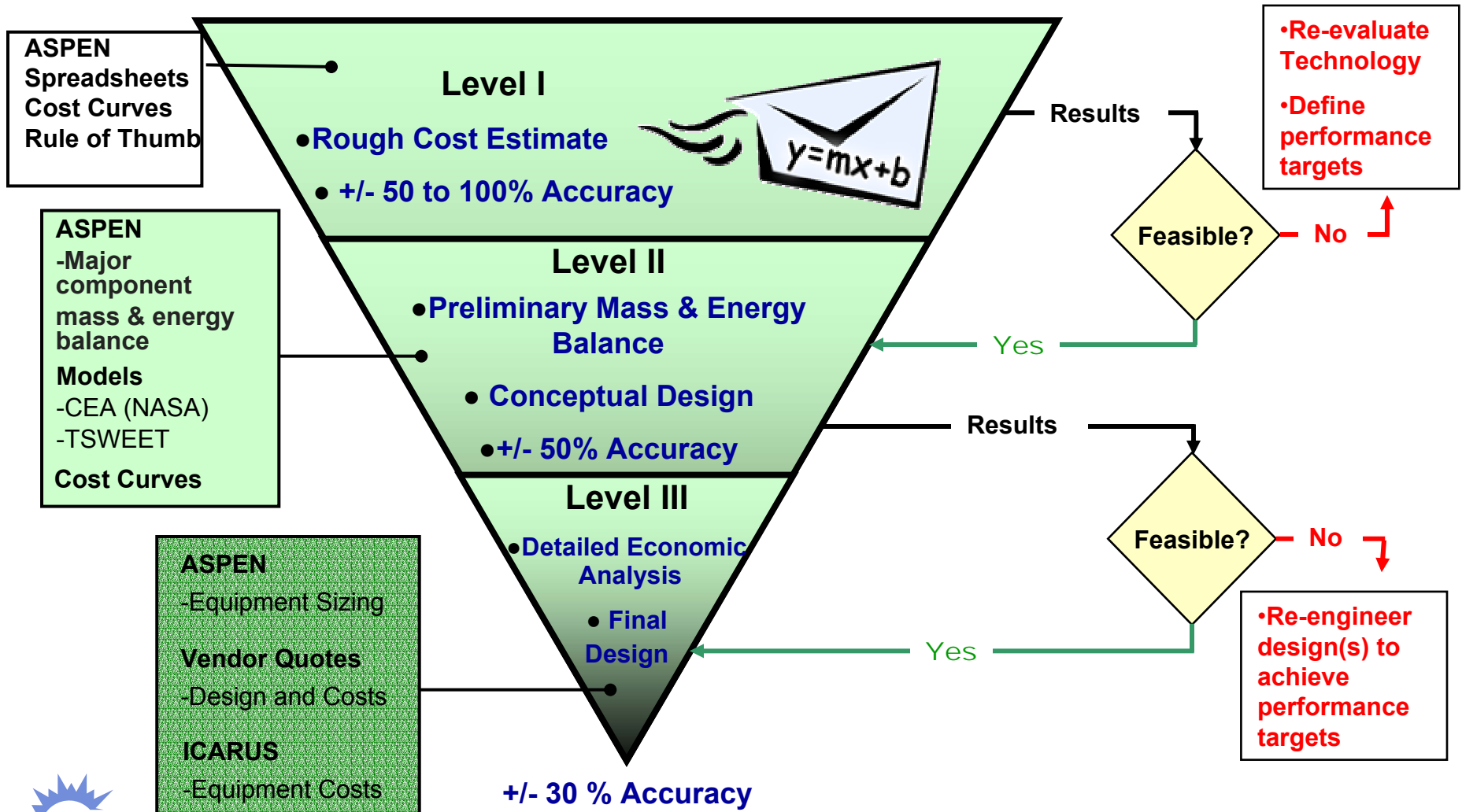
Economically
Feasible?

500 MW Commercial Power Plant



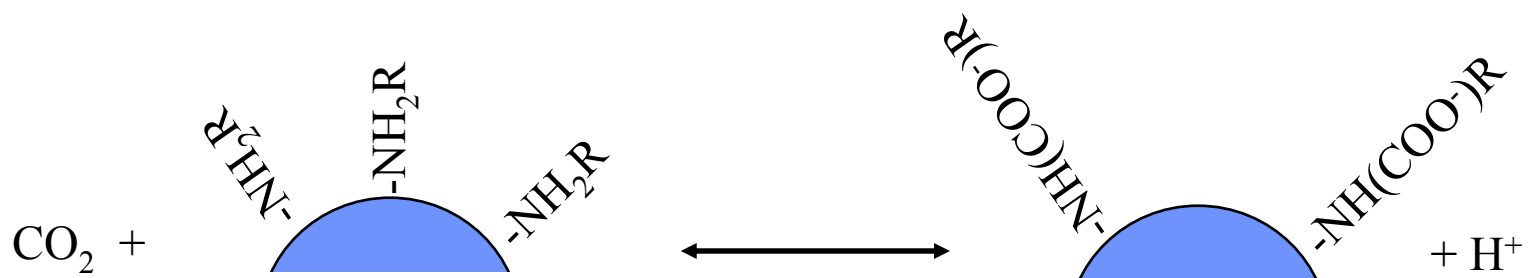
- 57,000 ft³ Reactor Volume
- 1,200,000 scf per minute

Systems Analysis Level of Detail



Amine Enhanced Sorbents

- Use the same type of amine chemicals as found in conventional wet scrubbers
- Amine molecules attached to solid pellets rather than dissolved in water



- **Substrate**
 - Meso-porous silica (SBA-15), PMMA, etc.
 - Amine binds to hydroxyl (-OH) sites on surface
- **Amine**
 - Testing primary, secondary, and tertiary

Amine Enhanced Sorbent Advantages

1. Uses less energy

- ↓ Heat Capacity (Do not need to heat water)
- Use less stripping steam to regenerate CO₂

Amine Enhanced Sorbents

Heat Capacity (Btu/lb-°F)	0.3
ΔT Regeneration	80°F
Regeneration Energy (Btu/lb CO ₂)	
Sensible	40
Reaction	+ 580*
Vaporization	+ 0
Total	= 620

VS.

30% MEA [1]

Heat Capacity (Btu/lb-°F)	0.9
ΔT Regeneration	105°F
Regeneration Energy (Btu/lb CO ₂)	
Sensible	941
Reaction	+ 703
Vaporization	+ 290
Total	= 1,934

Reference:

1. Gottlicher, G., *The Energetics of Carbon Dioxide Capture in Power Plants*, U.S. Department of Energy, National Energy Technology Laboratory, 1999

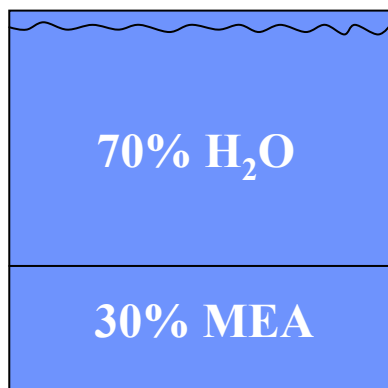


Amine Enhanced Sorbent Advantages

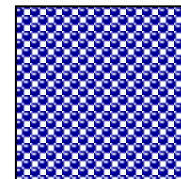
2. Higher CO₂ carrying capacity per lb of sorbent

	30% MEA	Amine Sorbent
Density (lb/ft ³)	22	44
Working Capacity (lb CO ₂ /lb sorbent)	0.052	0.264
Mass sorbent per pound CO ₂	19 lbs solution	3.8 lbs sorbent
Volume per Pound CO ₂ (ft ³ /lb CO ₂)	0.8	0.08

10x decrease in volume to treat equivalent amount of CO₂

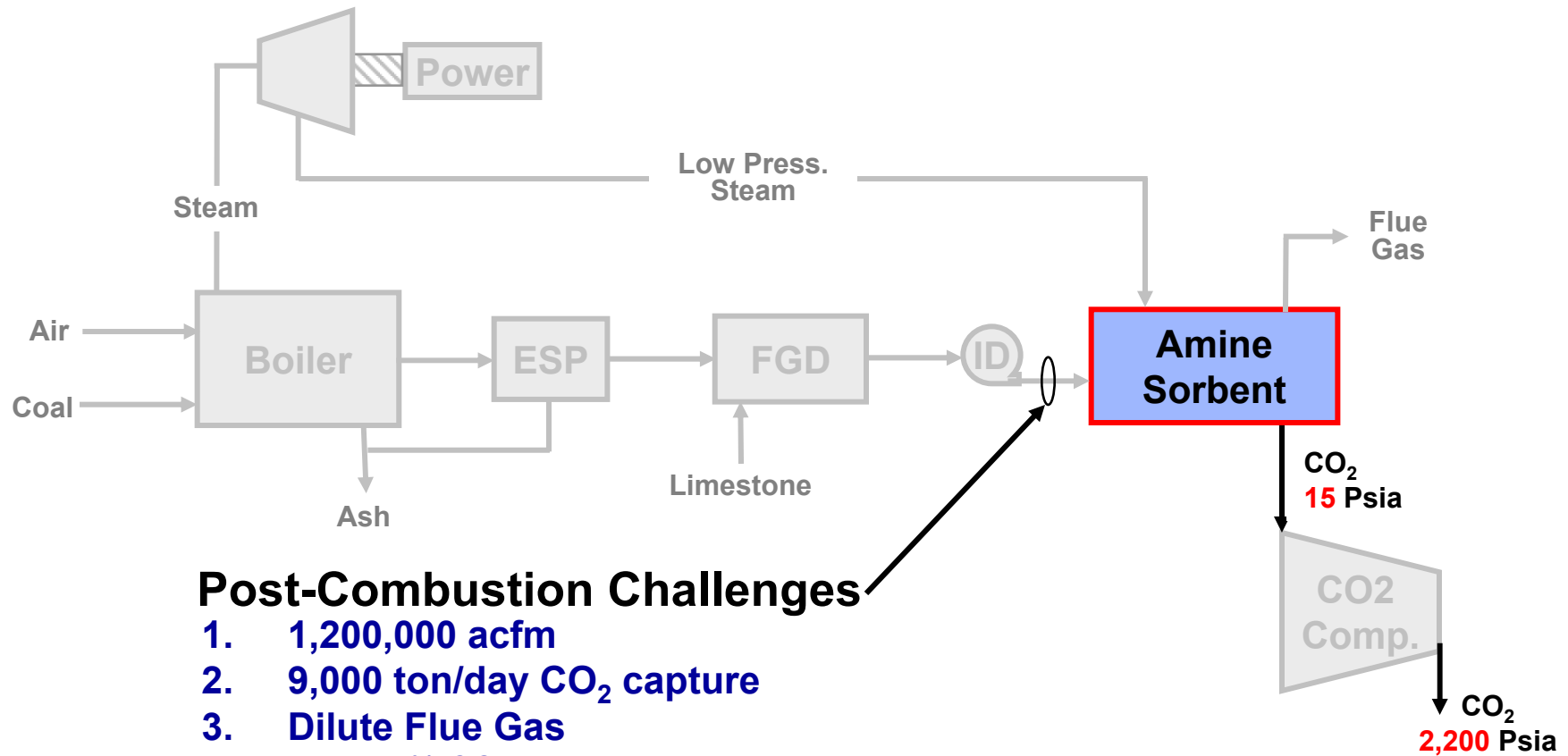


VS.



PC with Amine Enhanced Sorbent CO₂ Capture

Where does it fit?



Technical Approach

Overview

1. CO₂ Capture System Conceptual Design

- Model fixed and fluidized bed systems
 - *Standard mass and energy balance around CO₂ removal process*
 - *ΔP calculated from “Unit Operations of Chemical Engineering”, McCabe, Smith, and Harriot, 5th Ed.”*
 - *Perform heat integration and performance optimization*
 - *Preliminary absorber design based on boundary conditions*
- Calculate parasitic power load for CO₂ removal system
 - *CO₂ compression load*
 - *Lost power due to steam use in sorbent regeneration*
 - *Sorbent transport load*
 - *Fan load to overcome pressure drop*

2. Integrate CO₂ Capture system into existing plant

- Determine impact on plant performance (cost and efficiency)
- Spreadsheet approach → Uses existing power plant designs



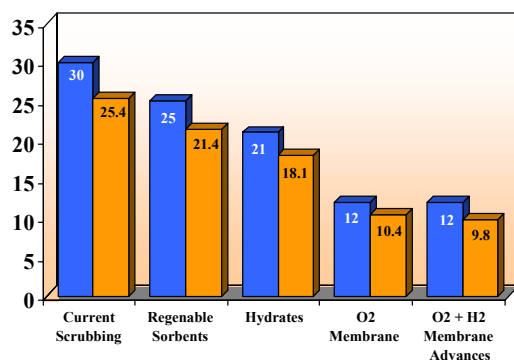
Technical Approach

Overview (continued)

3. Enter performance and cost data into NETL Economic Model

- EXCEL Spreadsheet based
- Builds on previous analyses and allows comparison with other technologies reviewed

4. Perform sensitivity analyses to optimize system design



Output

Section	Parameter	Case 1	Case 2	Case 3
Power Plant Input	Net Plant Size	424	387	400
	Fraction CO2 Recovered	80%	80%	80%
	Capacity Factor	85%	85%	85%
	On-site Power Plant Heat Rate	7880	7880	7880
	Wt% Mercury Control	0	0	0
CO2 Capture Input	Rated	0	0	0
	Wt% Requested with CO2	0	0	0
CO2 Compression & Drying Input	CO2 Compression & Drying	N/A	0	0
	Plant Compressor Inlet Pressure	0	0	0
	Plant Compressor Outlet Pressure	0	1,200	1,200
Land CO2 Transmission Input	Pipeline Distance (50-mile increments)	N/A	0	0
	Required Inlet Pressure (psi)	N/A	1,500	1,500
	Pipeline Outlet Pressure	N/A	1,200	1,200
	CO2 Temperature	N/A	77	77
	Pipe Diameter	N/A	32	32
Storage	Storage Type (EOR, 2-ECBM, 3-dense Form, 4-Sol)	N/A	0	0
	Storage Available Power	0	2.3	2.3
Auxiliary Power Output	Coal/Wing Handling	1.0	1.0	1.0
	Boiler/Fuel Recovery	1.0	1.0	1.0
	AUX	30.3	30.3	30.3
	Reboiler Use	0.0	0.0	0.0
	Net Plant	0.0	0.0	0.0



Technical Approach

Design Constraints

1. Flue gas flow rate of 1,200,000 acfm

- Based on a 400 MW_{net} Supercritical PC Plant
- 14 vol% CO₂
- 130° F, 14-17 psia

2. 90% CO₂ removal efficiency

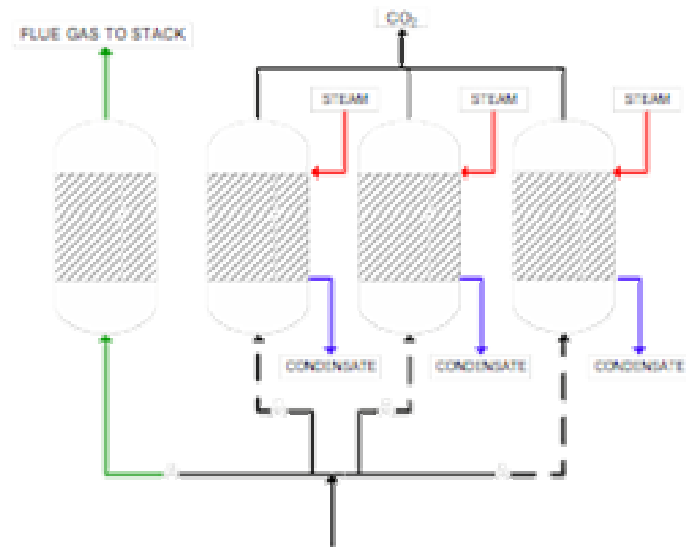
- DOE Program Goal
- Equates to 9,000 tons of CO₂ per day

3. Pressure drop of less than 6 psi

- Double that of MEA System

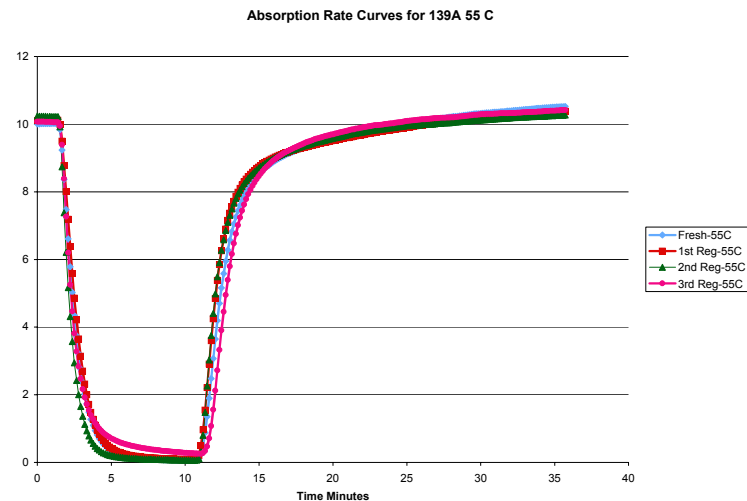
4. Geometry

- Maximum absorber diameter of 30 ft
- Maximum absorber height of 100 ft
- Footprint of less than 10,000 ft²



Amine Enhanced Solid Sorbent *Specification*

1. **SBA-15 Silica Substrate**
 - Particle Diameter: **50-100 μm**
 - Density: **2.6 g/cm^3**
2. **Capacity:** *6 moles CO_2 per kg sorbent*
3. **Cost Estimate:** *\$10/kg of sorbent*
4. **Regen Time:** *30-60 minutes*
5. **Operating Conditions**
 - Absorption: **120-160° F**
 - Regeneration: **230-250° F**
6. **Replacement:** *Every 2 years*



Challenges to Implementation

1. Pressure Drop....Pressure Drop.....Pressure Drop!

- Treating **1,200,000 acfm** of flue gas
- Capturing **9,000 Tons/day** of CO₂ (400 MW_{net} power plant)
- Sorbent diameter is very small: **50-100 μm**
- Result: Large pressure drop (6 psi) for short beds (12")

2. Regeneration Time

- **>30 minutes!** → Keep regeneration temperatures low to prevent loss of amine groups
- Results in large regeneration vessels

3. Sorbent cost and attrition rate

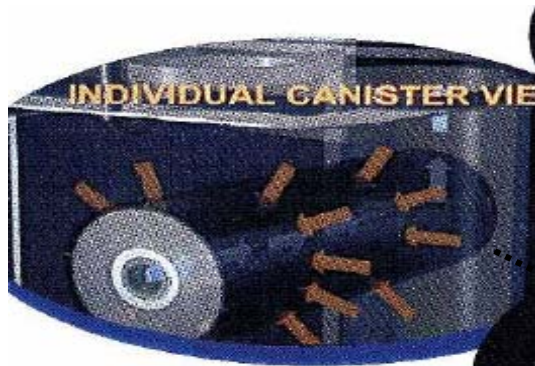
4. Heat management

- Absorption is exothermic
- Heat transfer in a fixed bed is poor



Novel System Design

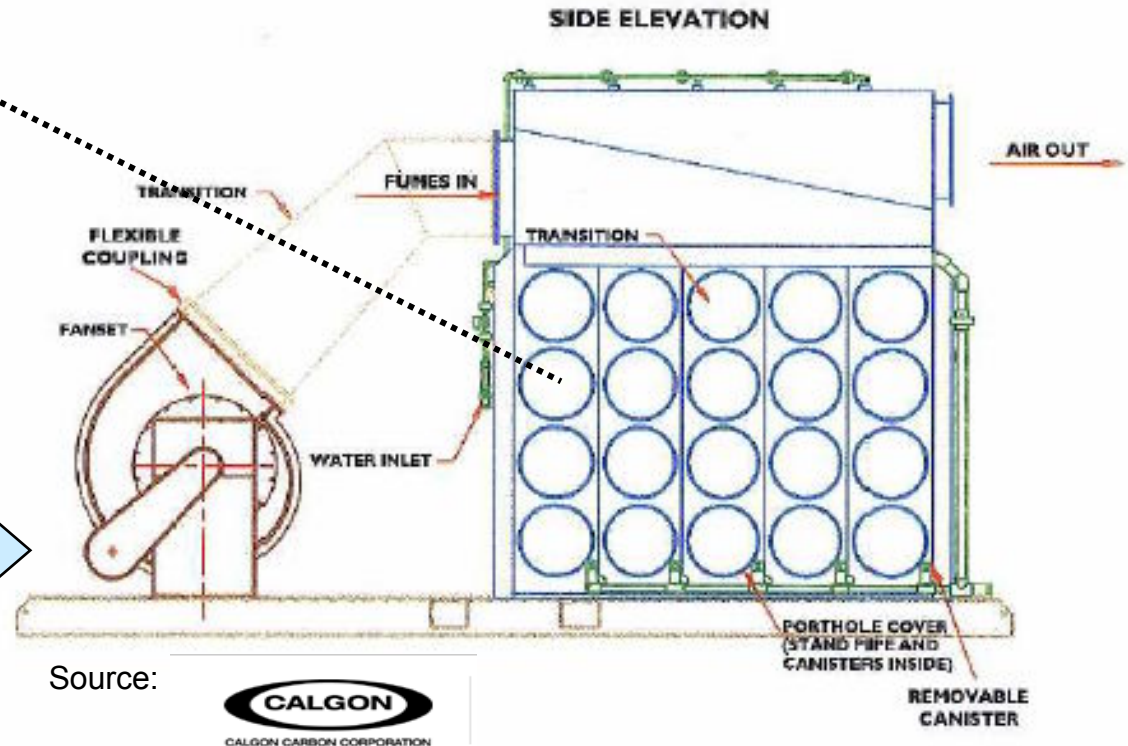
Explore other commercial absorber designs that deal with pressure drop problems.



Radial Flow Fixed-Bed Reactor

30,000 ft³/min
<0.5 psi drop!

Phoenix™
Calgon Carbon's High-Volume
Odor Control System



Source:



Design Results

Fixed Bed

- Large pressure drop (~6 psi)
- Large number of absorber vessels (50+)
- Very thin sorbent beds (< 26 inches)
- Large footprint unless units are stacked (~50,000 ft²)
- Chosen reactor geometry will not work
 - 30 ft diameter column with 26 inch bed height!

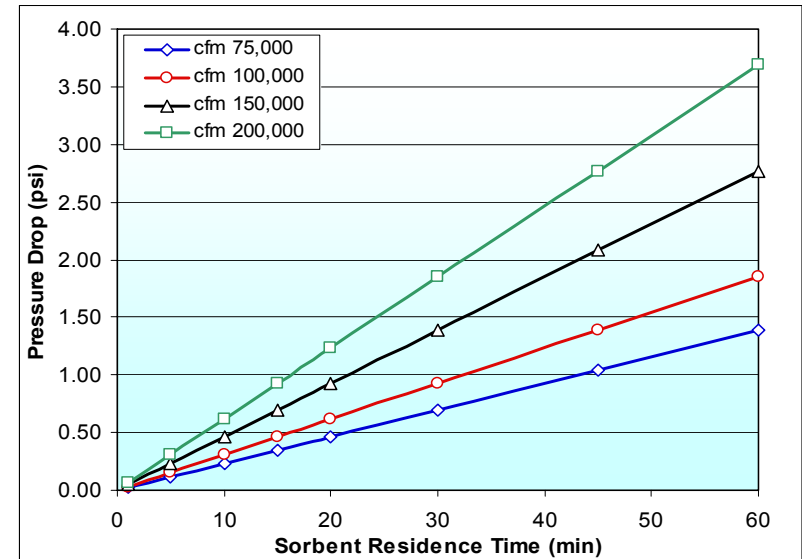
Flue Gas Flow Rate per Unit (acfm)	Max Bed Height (inches)	CO ₂ Capacity per Absorber (lbs)	T _{breakthrough} (mins)	Parallel Streams	Absorbers per Stream	Total Number of Absorbers	Total Sorbent Mass (tonnes)	Footprint (ft ²)
45,000	25.3	27,200	60	27	2	53	2,330	47,700
62,700	17.7	18,980	30	19	3	57	1,750	51,300
76,000	14.3	15,340	20	16	4	63	1,560	56,700
87,000	12.3	13,180	15	14	5	69	1,470	62,100
96,500	10.9	11,720	12	12	6	75	1,420	67,500
105,000	9.9	10,630	10	11	7	80	1,370	72,000
133,000	7.5	8,070	6	9	11	99	1,290	89,100
160,000	6.0	6,460	4	8	16	120	1,250	108,000
182,000	5.1	5,510	3	7	21	138	1,230	124,200



Design Results

Fluidized Bed

- **Small pressure drop**
 - ~0.5 psi
 - Function of solids residence time in the absorber
- **Footprint**
 - 7,000 ft²
 - Similar to wet-scrubbing system
- **Sorbent attrition rate**
 - Assume 6 month replacement
 - Increased O&M costs



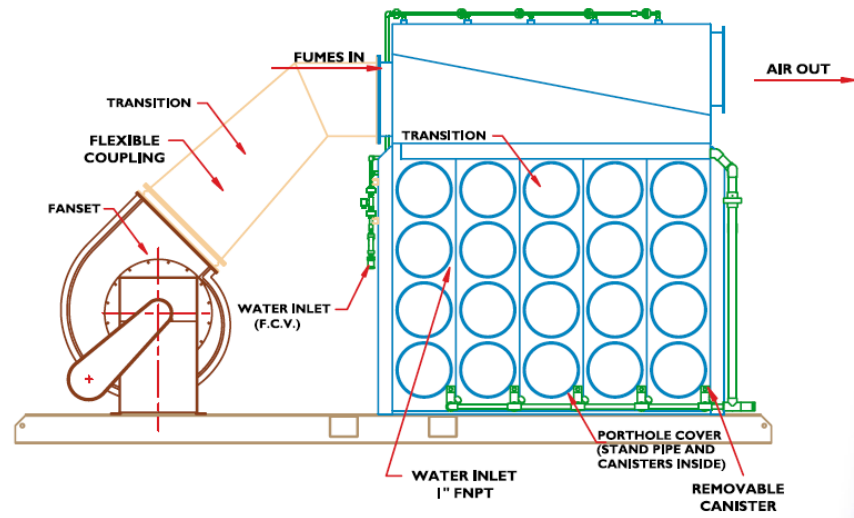
Flue Gas Flow per Unit (acfm)	# of Parallel Streams	Superficial Velocity (ft/s)	Sorbent per Absorber (tonnes)	Bed Height (inches)	Pressure Drop (psi)	Footprint (ft ²)
50,000	24	1.2	50	2	0.08	22,000
75,000	16	1.8	70	3	0.12	14,000
100,000	12	2.4	95	4	0.15	11,000
125,000	9.6	2.9	120	5	0.2	9,000
150,000	8	3.5	140	6	0.2	7,000
200,000	6	4.7	190	8	0.3	5,000



Design Results

Novel Design: Phoenix System

- Reasonable pressure drop
 - 3 psi
- Footprint
 - 10,000 ft²
 - Greater than wet-scrubbing system but within constraints
- No increased sorbent attrition rate



	Flowrate per Unit (acfm)	# of Absorption Units (Parallel Streams)	Sorbent Mass per Unit (tonnes)	Total Sorbent Mass Required (tonnes)	Pressure Drop (psi)	Total Footprint (ft ²)
Case 7	30,000	40	31	1,260	4.0	28,000
Case 8	50,000	24	52	1,260	3.2	25,000
Case 9	100,000	12	105	1,260	3.1	18,000
Case 10	150,000	8	165	1,320	2.9	11,000
Case 11	300,000	4	330	1,320	2.9	9,700



Design Results

Summary

- Fixed Bed System does not meet design constraints
- Fluidized Bed meets constraints but may have increased sorbent attrition
- Novel Fixed Bed meets constraints in certain configurations

	Flow Rate per Unit (acfm)	Absorber Units	Total Sorbent Mass Required (tonnes)	Pressure Drop (psi)	Total Footprint (ft ²)
Conventional MEA	250,000	8-10	N/A	3-6	5,000-9,000
Amine-Enriched Sorbent					
Fixed Bed	76,000	63	1,600	6	57,000
Fluidized Bed	150,000	8	1,100	0.3	7,000
Novel Fixed Bed					
Case 5	150,000	8	3,500	2.2	7,400
Case 11	300,000	4	1,300	2.9	9,700



Economic Analysis

Sorbent Capital Costs

- **Conventional MEA:** 2,700 lb/hr MEA make-up due to attrition
- **Fixed Bed Systems:** Sorbent replaced every 2 years
- **Fluidized Bed:** Sorbent replaced every 6 months

	Initial Sorbent Cost (MM \$)	Annual Sorbent Replacement Cost (MM \$ / yr)
MEA wet scrubbing*	\$94	\$8.1
Fixed Bed	\$15	\$7.5
Fluidized Bed	\$11	\$22
Novel Fixed Bed		
Case 5	\$35	\$18
Case 11	\$13	\$6.5

* MEA cost listed is total system cost



Economic Analysis

Plant Performance

	Pressure Drop (psi)	ID Fan Load (MW)	Solvent Pump Load (MW)	Gross Plant Size (MW)	Cost of Electricity (¢/kWh)	Cost of Electricity Increase
MEA Scrubber	3	22.4	3	491	7.56	55%
Fluidized Bed	0.3	6.5	N/A	465	6.88	41%
Novel Fixed Bed						
Case 5	2.2	15.9	N/A	474	6.93	42%
Case 11	2.9	19.4	N/A	478	6.34	30%

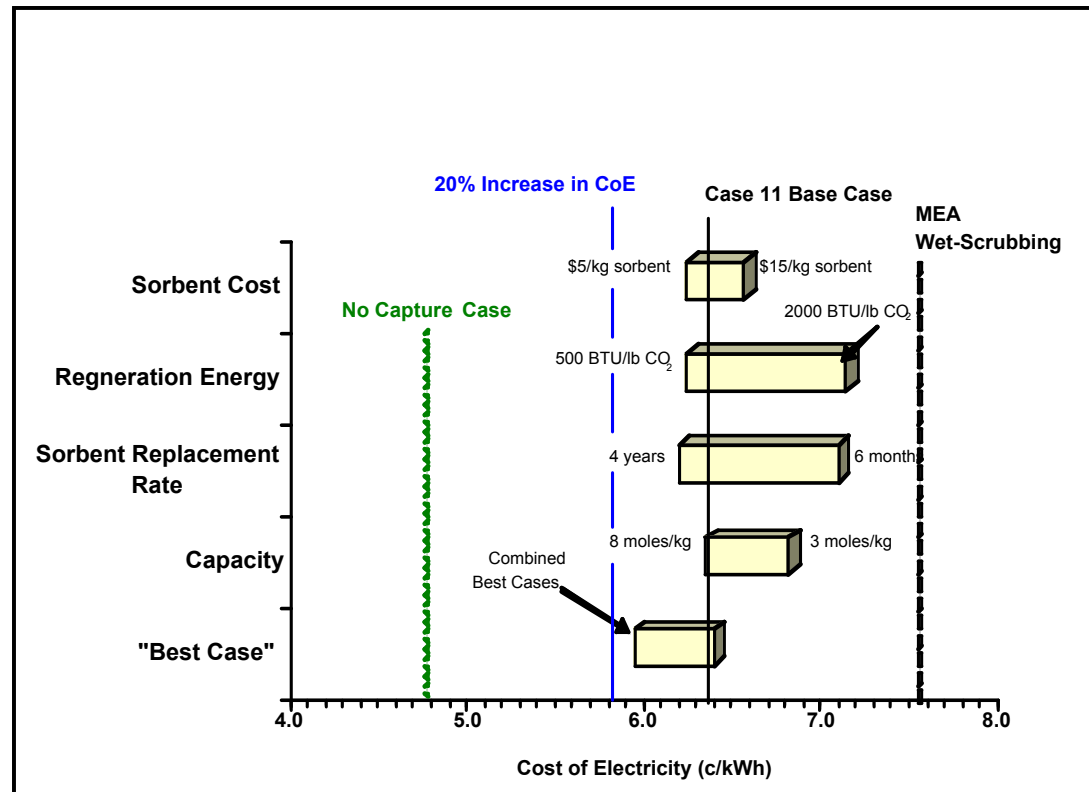
Solid sorbent CO₂ capture systems have a:

- 1. Smaller parasitic load (no solvent circulation)**
- 2. Smaller overall plant size**
 - Less steam required for regeneration means less coal burnt
 - Reduced parasitic load draws less power from
- 3. Reduced cost of electricity**
 - Smaller, more efficient plant
 - Reduced capital and O&M Costs



Economic Performance

Sensitivity Analysis



Property	"Best Case" Value	Baseline Variables	"Worst Case" Value
Sorbent Cost	\$5/kg sorbent	\$10/kg sorbent	\$15/kg sorbent
Regeneration Energy	500 BTU/lb CO ₂	620 BTU/lb CO ₂ [NETL]	2,000 BTU/lb CO ₂
Replacement Rate	Every 4 Years	Every 2 Years	Every 6 Months
Sorbent Capacity	8 moles CO ₂ /kg sorbent	6.4 moles CO ₂ /kg sorbent	3 moles CO ₂ /kg sorbent



Questions?



Pressure Drop Calculations

Ergun Equation:

$$\frac{\Delta P}{L} = \frac{150 \overline{V}_0 \mu (1 - \varepsilon)^2}{g_c \Phi_s^2 D_p^2 \varepsilon^3} + \frac{1.75 \rho \overline{V}_0^2 (1 - \varepsilon)}{g_c \Phi_s D_p \varepsilon^3}$$

$\Delta P \equiv$ Pressure drop across the fixed bed

$L \equiv$ Bed height

$\overline{V}_0 \equiv$ Superficial (empty tower) velocity

$D_p \equiv$ Sorbent particle diameter

$\mu \equiv$ Flue gas viscosity

$\varepsilon \equiv$ Volume fraction of void spaces in a bed of solids

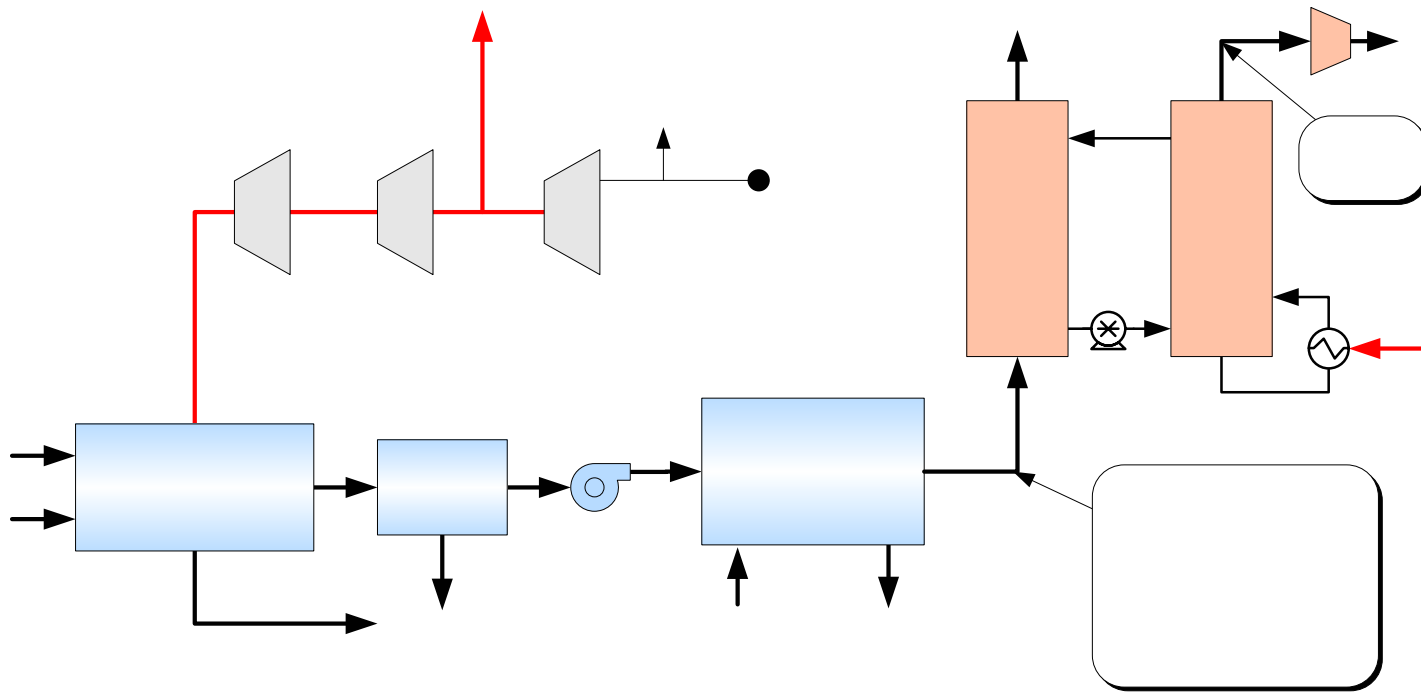
$\Phi_s \equiv$ Sphericity of sorbent

$\rho \equiv$ Flue gas density



Post-Combustion Current Technology

Pulverized Coal Power Plant with CO₂ Scrubbing



PhoenixTM Design “Assumptions”

First Glance

- **PhoenixTM System Parameters**
 - Canister Geometry
 - Canister Length: ~2’
 - Canister Diameter: ~14”
 - Sorbent Bed Thickness: ~4.5”
 - 50 ppm H₂S removal @ 30,000 acfm
 - 150 canisters
 - Parallel Operation: Only one bank regenerating at a time
- **Activated Carbon Parameters**
 - Diameter: 3.6 mm
 - Density: 0.56 g/cm³
 - Capacity: 0.055-0.09 g H₂S/cm³ carbon
 - 90-2900 minute regeneration time



System Differences

First Glance

	Species Concentration	Removal Rate	Sorbent Volume Required per minute of flow
H ₂ S Cleanup	50 ppm	9 lb/hr	1,240 cm ³ /min
CO ₂ Capture	10-13%	27,000 lb/hr	307,000 cm ³ /min

CO₂ Capture System Requires:

- ~3,000 times the absorption rate
- 250-400 times the sorbent volume
- 32 PhoenixTM units operating in parallel (30,000 cfm units)



Preliminary System Design

A Scaled-Up Phoenix System

	Number of Canisters	Sorbent Bed Thickness	Canister Diameter	Canister Length
Phoenix Unit	150	4.5"	1.2'	2'
Scaled-Up Phoenix Unit for CO ₂ Capture	320	6"	2.8'	6'

- **Increased canister size**
 - 3 times longer, 2.3 times greater diameter
- **Double the unit height**
 - Twice as many canisters per bank
- **One additional bank**
 - 20 additional canisters



Preliminary System Design

Scale-Up Results

- **Increased canister size lowers ΔP**
 - Increased sorbent volume at the same bed thickness
 - Increased surface area reduces linear velocity
 - Offset effects of smaller particle diameter
- **Increased unit height**
 - Utilizes available space
 - Reduces total system footprint
- **Additional bank**
 - Further reduces volumetric flow to any canister, and therefore linear velocity and pressure drop
 - Additional sorbent capacity



Preliminary System Design

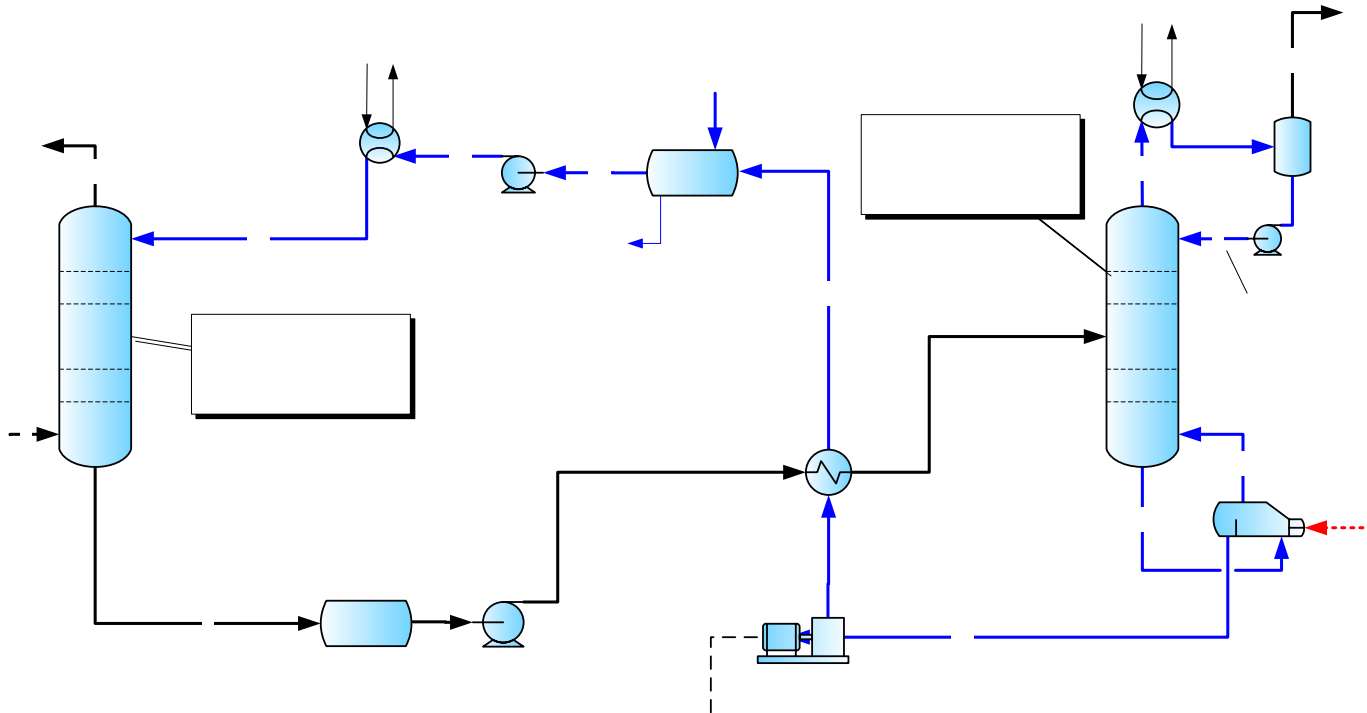
Results

- **Preliminary assessment of Phoenix™ System for CO₂ Capture looks promising**
- **Requires scale-up**
 - Increased adsorption rate
 - Increased sorbent volume required for same volumetric flow rate
- **Additional investigation is warranted and should be pursued!**



MEA Scrubbing Up-Close

2000 Baseline Case



Reboiler Heat Duty (Btu/lb CO ₂)	1,621	CO ₂ Rich Loading (mol CO ₂ /mol MEA)	0.441
MEA Concentration (wt. %)	27	CO ₂ Lean Loading (mol CO ₂ /mol MEA)	0.143
MEA Circulation Rate (GPM)	24,500	Scrubber/Stripper Pressure Drop (Psia)	3/3
Absorption (°F)	130's	Induced Draft Fan (MW)	15
Regeneration (°F)	250's	MEA Circulation Pumps (MW)	2



FG to Stack
135°F/15.4 Psia

30

Source: Case 7A from "Evaluation of Innovative Fossil Fuel Power Plants with CO₂ Removal", DOE/EPRI, 1000316

2

LA Recycle
100°F/65 Psia